High-performance solid oxide fuel cells based on a thin $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolyte membrane supported by a nickel-based anode of unique architecture

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Abstract

Solid oxide fuel cells (SOFCs) based on a thin $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) electrolyte membrane supported by a nickel-based anode often suffers from undesirable reaction/diffusion between the Ni anode and the LSGM during high-temperature co-firing. In this study, a high performance intermediate-temperature SOFC is fabricated by depositing thin LSGM electrolyte membranes on a LSGM backbone of unique architecture coated with nano-sized Ni and $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC) particles via a combination of freeze-drying tape-casting, slurry drop-coating, and solution infiltration. The thickness of the dense LSGM electrolyte membranes is $\sim 30\text{ }\mu\text{m}$ while the undesirable reaction/diffusion between Ni and LSGM are effectively hindered because of the relatively low firing temperature, as confirmed by XRD analysis. Single cells show peak power densities of $1.61\text{ W}\cdot\text{cm}^{-2}$ at 700°C and $0.52\text{ W}\cdot\text{cm}^{-2}$ at 600°C using 3 vol% humidified H_2 as fuel and ambient air as oxidant. The cell performance is very stable for 115 h at a constant current density of $0.303\text{ A}\cdot\text{cm}^{-2}$ at 600°C .

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1. Introduction

Solid oxide fuel cells (SOFCs) have attracted great attentions as alternative power generation systems due to their high energy conversion efficiency, low pollutant emission, and excellent fuel flexibility [1-6]. Ytria-stabilized zirconia (YSZ) is the most commonly used electrolyte due to its nearly pure oxygen ionic conductivity and excellent mechanical properties. However, its relatively low ionic conductivity at intermediate temperature (500-700°C) is a bottleneck inhibiting the development for intermediate temperature SOFCs. Therefore, several alternative electrolytes with high ionic conductivity at intermediate temperature have been explored, including doped ceria ($\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$, GDC) [7], doped BaCeO_3 ($\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$, $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$) [8] and doped LaGaO_3 ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$, LSGM) [9, 10]. However, doped ceria tends to be partially reduced at elevated temperatures and low oxygen partial pressure, resulting in electronic conductivity which leads to a reduction of the open-circuit voltage (OCV) and thus an energy loss [11]. Meanwhile, even though doped BaCeO_3 materials possess high proton conductivities at low temperatures, their tendency to react with H_2O and CO_2 in the atmosphere may result in electrolyte degradation [12, 13]. Among these potential materials, more conductive LSGM electrolyte has been extensively studied as a promising electrolyte material because of its superior oxygen-ion conductivities at intermediate temperatures over a broad range of oxygen partial pressures [9, 14].

To date, the high cost associated with the fabrication of thin LSGM membranes and the undesirable reactions between LSGM and the anode catalyst Ni during high-

temperature co-firing process made it difficult the fabrication of SOFCs based on a thin LSGM electrolyte membrane supported by a Ni-based anode. To restrain the undesirable reactions, a lanthanum-doped ceria (LDC) buffer layer was often introduced to form a LDC/LSGM bilayer [15] or LDC/LSGM/LDC tri-layer structure [16]. However, a thin LDC layer may not be effective for avoiding Ni diffusion into the LSGM electrolyte, while a thick LDC layer may result in a large cell ohmic resistance. Bozza et al. [17] had successfully fabricated thin LSGM membranes without LDC buffer layer on LDC anode backbone avoiding the undesirable reactions between LSGM and Ni by firstly co-firing LSGM electrolyte/LDC anode bilayer at high temperature and then infiltrating Ni(III) salt into LDC anode backbone. But the conventional sponge-like (random microstructure) porous LDC anode substrate fabricated by tape-casting is not ideally suited for ion-infiltration and gas diffusion because of the high tortuosity factor, consequently limiting the cell performance. In our previous work [18-21], we have reported an anode of unique architectures with hierarchically open and straight porous network by freeze-drying tape-casting, significantly facilitating gas diffusion, thus enhancing the cell performance. This anode of novel architecture is also ideally suited for infiltration of catalysts using a solution infiltration process [22].

In this study, porous LSGM anode backbones with straight open pores/channels were fabricated using a freeze-drying tape-casting process to avoid undesirable reaction/diffusion between the LSGM electrolyte and the Ni-based anode and to facilitate infiltration of catalysts and gas diffusion. The LSGM anode backbone/LSGM electrolyte bilayer was fabricated by drop-coating and co-firing, with subsequently screen-printing the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) cathode on the electrolyte and infiltration of nickel-

based anode into the porous LSGM anode backbone. The as-prepared cells demonstrated excellent performance and good short-term stability at intermediate temperatures.

2. Experimental

2.1 Fabrication of anode substrate and cells

LSCF and LSGM powders (both from Fuel Cell Materials, USA), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (all from Alfa Aesar, USA) were purchased for this study. Open and straight porous LSGM backbone was prepared by a freeze-drying tape-casting process as reported in our previous study [18, 21]. The frozen LSGM support was punched into pellets with diameter of about 15 mm and dried under a vacuum of 100 mtorr at -30°C . The dried LSGM supports were placed at room temperature, and then the LSGM slurry was directly deposited on the green LSGM anode supports by drop coating. The LSGM anode backbone/LSGM electrolyte bilayer was then co-fired at 1450°C for 12 h, with a heating rate $1^\circ\text{C}/\text{min}$ before 600°C and $2^\circ\text{C}/\text{min}$ after 600°C . The LSCF slurry was screen-printed onto the top of the LSGM electrolyte layer, followed by firing at 1080°C for 2 h to form porous LSCF cathode. The effective area of the cathode was 0.33 cm^2 .

The porous LSGM anode substrate of the single cells was then infiltrated using aqueous solution of $\text{Gd}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_2$ with a weight ratio 50:50 wt% of $\text{NiO-Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC), followed by drying in an oven at 60°C for 12 h and firing at 800°C , resulting in a coating layer of NiO-GDC particles on the surfaces of LSGM anode backbone, forming NiO-GDC-LSGM anode. This cycle was repeated 4 times until a NiO-GDC loading level of 6 wt% was achieved.

2.2 Characterization

Phase identification of the electrolyte film and infiltrated anode was carried out using an X-ray diffractometer (Pert PRO Alpha-1). The cross-sectional view of the single cells and the surface of the LSGM electrolyte film and anode substrate were characterized using a scanning electron microscope (SEM, Zeiss Ultra plus FESEM). The current density-voltage curves and electrochemical impedance spectra (EIS) of the cells were measured with a four probe method using a multi-channel Versa STAT (Princeton Applied Research) at the operating temperatures ranging from 600°C to 700°C. NiO paste and silver paste were employed as current collectors on the anode and the cathode side, respectively. Silver wires were used as the lead wires. During cell measurement, humidified H₂ (with 3 vol% H₂O) was used as the fuel while the cathode side was exposed to ambient air. Gas flow rate of H₂ was controlled at 40 sccm by a precision volume flow controller (APEX, Alicat Scientific). The cells were first stabilized at 700°C to allow complete reduction of NiO to Ni. The EIS was performed under open circuit condition with 10 mV AC amplitude and the frequency range of the measurement was from 1 MHz to 0.1 Hz. The short-time stability of the cells using H₂ as fuel was examined under a constant current density of 0.303 A·cm⁻² at 600°C.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of a thin LSGM electrolyte membrane supported by a porous LSGM backbone infiltrated with NiO and GDC nanoparticles. All the peaks can be attributed to the pure perovskite structure. As shown in Fig. 1(b), all the peaks of the infiltrated anode correspond to NiO, GDC, and LSGM phases without other phases or impurities, indicating that the diffusion/reaction between Ni and the LSGM electrolyte or

between Ni and the LSGM anode backbone has been effectively hindered because of the relatively low firing temperature during the anode preparation process.

Shown in Fig. 2(a) is a cross-sectional image of the as-prepared cell. The cell has an open-structured LSGM anode layer, a thin dense LSGM electrolyte ($\sim 30\text{ }\mu\text{m}$), and a porous LSCF cathode layer ($\sim 20\text{ }\mu\text{m}$). The dense LSGM electrolyte film adheres well to the anode and the cathode. Fig. 2(b) shows the surface morphology of the as-prepared LSGM membrane on the anode support. It can be seen that the LSGM membrane is crack-free, continuous, and quite dense with grain size of 6-12 μm . The dense LSGM electrolyte membrane may be responsible for the high OCV as to be described later. The microstructures of the infiltrated anode are shown in Fig. 2(c) and (d). After infiltration, a uniform and thin layer of NiO-GDC nano-sized particles are sufficiently coated on the LSGM anode backbone, indicating that the novel LSGM anode backbone architecture is beneficial for infiltration of NiO and GDC.

The electrochemical performance of the as-prepared cells is obtained at operating temperatures of 600°C to 700°C with humidified H_2 as the fuel and ambient air as the oxidant. As shown in Fig.3(a), the OCV values of the cell were 1.121, 1.108, and 1.105 V at 600°C, 650°C, and 700°C, respectively, which are much higher than those of the anode-supported cells with SDC electrolyte (e.g., 0.901 V at 600°C) [23], and similar to the cells based on the LSGM electrolyte fabricated by electrophoretic deposition (EPD) or pulsed laser deposition (PLD)[17, 24]. The high OCV values showed that the LSGM electrolyte film fabricated by drop-coating process was sufficiently dense, consistent with the SEM images in Fig. 2 (a) and (b). The peak power densities are $0.52\text{ W}\cdot\text{cm}^{-2}$ at 600°C, $0.99\text{ W}\cdot\text{cm}^{-2}$ at 650°C, and $1.61\text{ W}\cdot\text{cm}^{-2}$ at 700°C, respectively, much higher (almost

twice) than the values reported by others for the cells based on LSGM electrolyte with LSCF cathode but with a conventional sponge-like porous anode coated with NiO [17]. Zhan et al. [25] also reported a similar work through infiltrating Ni solution into the sponge-like LSGM backbone, and the cells showed a power density of $1.21 \text{ W}\cdot\text{cm}^{-2}$ at 650°C higher than the values reported in this work. The bilayer cathode consisting of LSCF-LSGM / LSCF, and finer NiO grain size (15-45 nm) in that work may contribute to the higher cell performance. One thing worth mentioning is that infiltrating catalyst solution into anode is an effective way to avoid undesirable reaction/diffusion between LSGM electrolyte and anode as well as to fabricate high performance cells, and the open-structured anode adopted in the current work shows an advantage of efficient ion-infiltration. Fig. 3(b) shows the impedance spectra of the cells measured at different temperatures under open circuit conditions. The spectra interception with the real-axis in low frequencies represents the total resistance (R_t) of the cell, including ohmic resistance (R_{ohm}) and interfacial polarization resistance (R_p). The cell ohmic resistance (R_{ohm}) is the spectra interception with the real-axis at high frequencies, while the polarization resistance (R_p) is the difference between R_t and R_{ohm} . The R_{ohm} of the cell is $0.23 \text{ }\Omega\cdot\text{cm}^{-2}$ at 600°C , $0.12 \text{ }\Omega\cdot\text{cm}^{-2}$ at 650°C , and $0.10 \text{ }\Omega\cdot\text{cm}^{-2}$ at 700°C , lower than cells with LDC (10 μm) /LSGM (9 μm)/LDC (10 μm) tri-layer electrolyte ($0.19 \text{ }\Omega\cdot\text{cm}^{-2}$ at 650°C , $0.12 \text{ }\Omega\cdot\text{cm}^{-2}$ at 700°C) [16]. The low R_{ohm} value in the present work may be attributed to the thin LSGM electrolyte membrane without the LDC buffer layer. The measured polarization resistance is $1.76 \text{ }\Omega\cdot\text{cm}^{-2}$ at 600°C , $0.64 \text{ }\Omega\cdot\text{cm}^{-2}$ at 650°C , and $0.38 \text{ }\Omega\cdot\text{cm}^{-2}$ at 700°C , respectively. In our previous work [20, 21], the anode microstructure with open and straight pores/channels has been reported to own advantages on facilitating gas

diffusion to the anode/electrolyte interface as well as water vapor diffusion away from the anode/electrolyte interface, thus minimizing the loss due to mass transport through the porous electrodes. Therefore, lower polarization resistances will be anticipated by a combination of open-structured anodes and optimizing weight ratio of NiO and GDC in infiltrating solution as well as infiltration content.

Shown in Fig. 4 is the short-term stability test of the test cells under a constant current of $0.303 \text{ A}\cdot\text{cm}^{-2}$ at 600°C using humidified hydrogen (3 vol% H_2O) as fuel. The cell with infiltrated NiO-GDC-LSGM anode shows very stable cell performance in H_2 for 115 h. The stable cell performance may be attributed to the nano-sized NiO-GDC coating layer by enhancing the kinetics of hydrogen oxidation as well as limited Ni grain growth because of the presence of the GDC nano-particles [26].

4. Conclusions

A high-performance intermediate-temperature solid oxide fuel cell based on a thin LSGM electrolyte membrane supported by an anode of unique architecture has been fabricated. The undesirable reaction/diffusion between LSGM electrolyte and Ni was effectively avoided by co-firing LSGM electrolyte and LSGM anode backbone before infiltrating Ni particles. Dense LSGM electrolyte membranes were successfully fabricated by a simple and cost-effective drop-coating process, resulting in OCV values higher than 1.1 V. The porous anode support with open pores/channels fabricated by freeze-drying tape-casting was ideally suited for fast gas diffusion and easy infiltration of NiO and GDC, thus enhancing cell performance. The as-prepared cells showed peak power densities of $1.61 \text{ W}\cdot\text{cm}^{-2}$ at 700°C and $0.52 \text{ W}\cdot\text{cm}^{-2}$ at 600°C using H_2 as fuel and ambient air as oxidant, much higher than those of the cells based on thin LSGM

electrolyte membranes supported by a randomly porous anode [17]. In addition, the cells showed a stable cell performance in H₂ for 115 h under a constant current density of 0.303 A·cm⁻² at 600°C.

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Fig.1

Fig. 2

Fig. 3(a)

Fig. 3(b)

Fig. 4

Figure captions

Fig.1 XRD patterns of (a) the LSGM electrolyte membrane supported by the anode and (b) the anode infiltrated with NiO and GDC.

Fig.2 SEM images of (a) a cross-section view of the as-prepared anode supported cell, (b) surface view of the LSGM electrolyte membrane, (c) low-magnification and (d) high-magnification images of the anode infiltrated with NiO and GDC near the electrolyte membrane.

Fig.3 (a) Electrochemical performance of the as-prepared cell with humidified hydrogen at different temperatures

Fig.3 (b) Impedance spectra of the as-prepared cell with humidified hydrogen at different temperatures

Fig.4 The short-term stability of as-prepared cells under a constant current of $0.303 \text{ A}\cdot\text{cm}^{-2}$ tested at 600°C using humidified hydrogen as fuel.